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The reactions of lithium trimethysilylmethyls with isocyanides; structures and reactions of the derived lithium 1-azaallyls, β-diketiminates and a 1-azabuta-1,3-dienyl-3-amide

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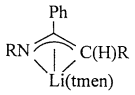
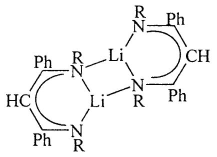
The insertion of ArNC (Ar = 2,6-$Me_2C_6H_3$) or Bu^tNC into the Li–C bond of [Li{C(H)(R)R′}] (R = $SiMe_3$, R′ = R or Ph) led to (i) the lithium 1-azaallyls [Li{N(R″)C(R)C(H)R′}(tmen)] (**6a** R′ = R, R″ = Ar; **6b** R′ = Ph, R″ = Ar; **6c** R′ = Ph, R″ = Bu^t), (ii) the lithium β-diketiminates [Li{N(Bu^t)C(R)C(H)C(R)NBu^t}][($LiCHR_2$)($CNBu^t$)] **1**, Li{N(Ar)C(R)C(H)C(R)N(Ar)} **2** and [Li{N(Ar)C(R)C(H)C(Ph)N(R)}(tmen)] **7** (from **6a** and PhCN), or (iii) the lithium amide [Li{N(Ar)C(R)C[N(Ar)]=C(H)Ph}(tmen)] **8**. Treatment of the lithium β-diketiminates **1** and **2** with $ZrCl_4$ yielded the complexes [$ZrCl_3${N(Bu^t)C(R)C(H)C(R)NBu^t}] **3** or [Zr{N(Ar)C(R)C(H)C(R)N(Ar)}Cl_2(μ-Cl)$_2$-Li(OEt_2)$_2$] **4**, while reaction of the lithium compounds **2** or **8** with MeOH gave in high yield the conjugate acids of the corresponding anions [HN(Ar)C(R)C(H)C(R)NAr] **5** or [HN(Ar)C(R)C{N(Ar)}=C(H)Ph] **9**. Each of the compounds **1**–**9** was fully characterised by multinuclear NMR spectroscopy, mass spectrometry and microanalysis, while X-ray diffraction data are also provided for the complexes **4**, **6b** and **8**.

Reactions between a lithium alkyl LiR′ and an isocyanide R″NC have been investigated in considerable detail. They provide a convenient source for synthesising aldehydes,[1,2] ketones,[1,2] α-hydroxy-ketones,[1–4] β-hydroxy-ketones,[2] β-hydroxy-acids,[1] α-keto-acids,[1,5] α-amino-acids[6] or heterocycles such as [R(R′)COC(H)=NC(H)(R″)][7] or [N=C(R)X{1,2-C_6H_4}] (X = S, PPh, $SiMe_2$, $GeMe_2$, $SnMe_2$).[4] The lithio aldimine LiC(R′)=NR″ (a masked carbanion) was postulated to be an intermediate, but has not been isolated.[1,2,4–6,8]

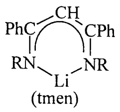
Our interest in this type of behaviour derives from (i) our earlier studies on the reactions between a lithium trimethylsilylmethyl and an α-H-free nitrile to give lithium 1-azaallyls (*e.g.* **A**), β-diketiminates (*e.g.* **B** or **C**) or 1,3-diazaallyls (*e.g.* **D**) (R = $SiMe_3$); and (ii) the observation that metal complexes containing a bound isocyanide react with a halogenoalkane to give C–C-coupled products. As for (i), examples include reactions between $LiCHR_2$ and PhCN affording **A**–**D** and C_6H_4-[C(H)(R)Li(tmen)]$_2$-1,2 **E** and Bu^tNC yielding **F**.[9] Regarding (ii), illustrations are shown in eqns. (1)[10] and (2).[11]



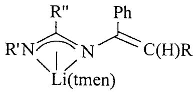
A



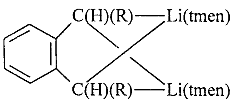
B



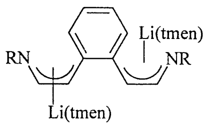
C



D (R' = R,R''=Ph)
D' (R'=Ph,R''=R)

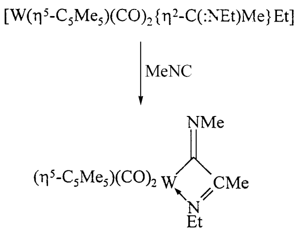


E



F

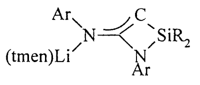
$$SmI_2 \xrightarrow[2.\ EtBr\ (Ar = 2,6\text{-}Me_2C_6H_3)]{1.\ ArNC,\ hmpa,\ thf} \underset{\text{not isolated}}{SmI_2\{C(:NAr)Et\}} \xrightarrow[2.\ H_2O]{1.\ ArNC} Et[C(:NAr)]_2H \qquad (1)$$



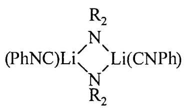
(2)

As an extension of our research on nitriles, such as those of (i) above, we turned our attention to isocyanide reactions with lithium alkyls,[12] silyls[13] or amides[14] containing one or more β-trimethylsilyl substituents. Thus treatment of isocyano-2,6-dimethylbenzene (≡ ArNC) with [Li(SiR_3)(thf)$_3$] or PhNC with $LiNR_2$ gave the crystalline 4-aryl(lithio)amino-1-aza-2-silacyclobut-3-ene **G**[13] or the dimeric 1 : 1 adduct **H**,[14] respectively.

Relevant to the present paper, we have previously shown that **A** with isocyanobenzene yielded the 1,3-diazaallyllithium compound **D′**.[9] Moreover, in 1998 we briefly communicated our



G



H

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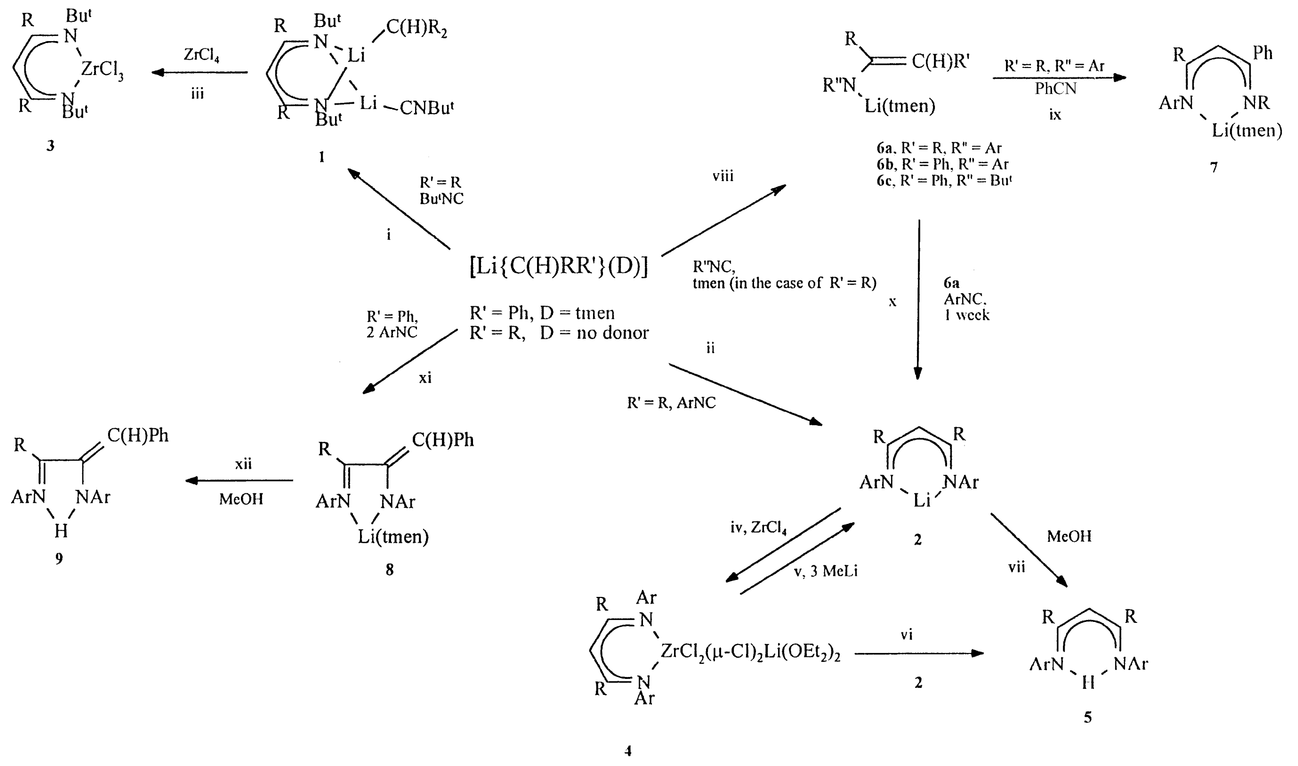
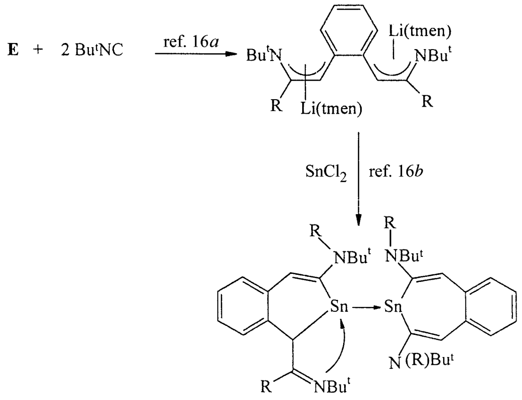


Scheme 1

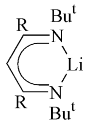
initial findings on the reactions of $LiCHR_2$ with 2-isocyano-2-methylpropane (affording **1**) or ArNC (giving **2**).[12] This paper provides full details of that report[12] and provides significant elaborations, encompassing the synthesis and characterisation of eight additional new compounds **3**–**9** (Scheme 1). In the interim, publications in 2000 by Leung and co-workers have revealed reactions between the dilithium compound **E**[15] and Bu^tNC, eqn. (3);[16] both the crystalline lithium[16a] and the tin[16b] complexes were X-ray-characterised.



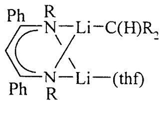
(3)

Results and discussion

The reaction of $LiCHR_2$ with Bu^tNC or ArNC in diethyl ether at low temperatures yielded (i or ii in Scheme 1) the lithium β-diketiminate complexes: the yellow **1** and the orange **2** (see also ref. 12). Although **1** is unusual in being a 1 : 1 : 1 adduct of $LiCHR_2$, $Li\{N(Bu^t)C(R)C(H)C(R)NBu^t\}$ **I** and Bu^tNC, conceptually it has a skeletal precedent in the X-ray-characterised complex **J** (obtained from $LiCHR_2$ and PhCN in thf).[9,12] It is noteworthy that **1** proved to be unreactive towards heat or excess of Bu^tNC (which might have been expected to yield the free lithium β-diketiminate **I**). Reaction of **1** or **2** with an equivalent portion of zirconium(IV) chloride gave (iii or iv in Scheme 1) in good yield the yellow, crystalline β-diketiminatozirconium(IV) complexes **3** or **4**, respectively. Complex **4** is unusual in being a heterobinuclear complex of a type more frequently found in Group 3 and lanthanide chemistry, originally in $[Y\{\eta^5\text{-}C_5H_4(SiMe_3)\}_2(\mu\text{-}Cl)_2Li(thf)_2]$;[17] although examples in zirconium chemistry are shown in **K**,[18a] **K'**[18b] and **K''**,[18c] for which, as for **4**, the role of LiCl is presumed to be to coordinatively saturate the zirconium environment of the otherwise labile LiCl-free complex. Attempts to displace one or more of the chloride ligands of **4** by treatment with methyllithium led (v in Scheme 1) instead to the isolation of **2** and, judged by its appearance, zirconium metal. Similarly, substitution of a chloride ligand of **4** by a β-diketiminate did not succeed; the only isolated product was (vi in Scheme 1) the yellow β-diketimine **5**. The latter was more rationally obtained (vii in Scheme 1) by protonolysis of **2** using methanol.



I



J

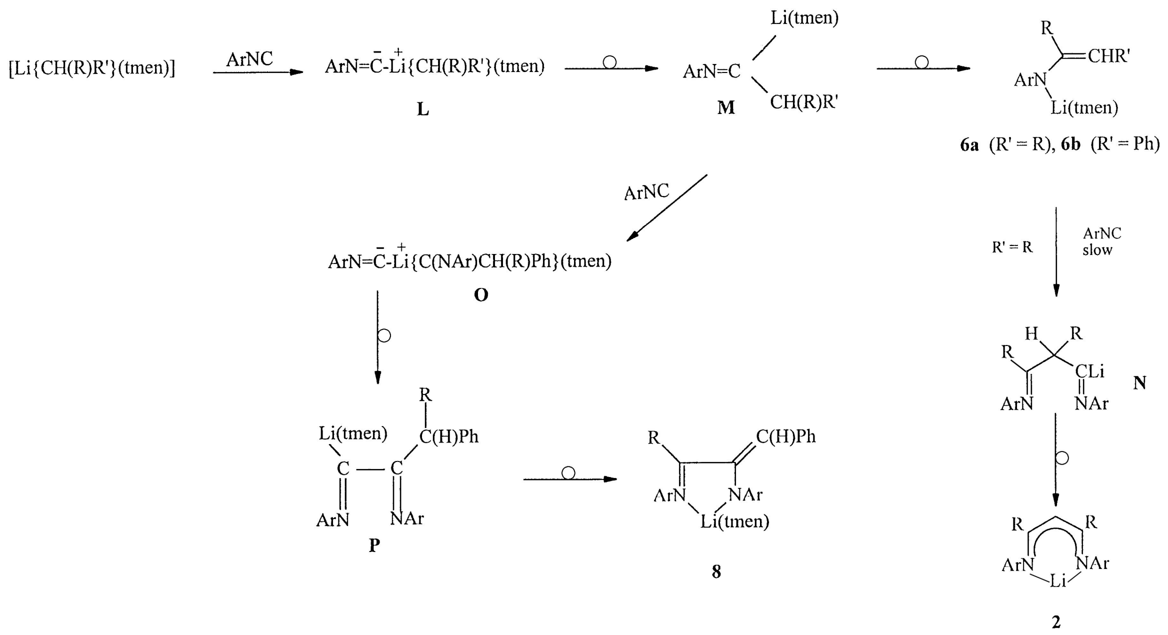
$[ZrX(X')(X'')(\mu\text{-}Cl)_2Li(OEt_2)_2]$

K[18a] $X = X' = OCBu^t_3$, $X'' = Cl$

K'[18b] $X(X')(X'') = \{N(C_6H_4F\text{-}2)SiMe_2\}_3CH$

K''[18c] $X = \eta^5\text{-}C_5H_5$, $X'X'' = \eta^5\text{-}C_4H_4BNPr^i_2$

Whereas $LiCHR_2$ with ArNC in the absence of a strong neutral donor had yielded the 1 : 2 adduct, the lithium β-diketiminate **2**, introduction of tmen afforded (viii in Scheme 1) the 1 : 1 adduct, the red lithium 1-azaallyl **6a**; similarly, the yellow analogue **6b** or **6c** was obtained from $[Li\{CH(R)Ph\}(tmen)]$ and ArNC or Bu^tNC, respectively. The role of tmen (or a similar strong neutral coligand) in the related $LiCHR_2$–PhCN reactions had previously been noted, the product having been **A** or, in the absence of such a coligand, **B**.[9] With ArNC or Bu^tNC complex **6a** was converted (x or ix in Scheme 1) into the lithium β-diketiminate **2** (in a slow reaction) or the orange **7**, respectively. While each of the above compounds **1**–**7**, based on



Scheme 2

$\mathrm{Li\{CH(R)R'\}}$ (R′ = R or Ph) as precursor, was a 1-azaallyl or β-diketiminate derivative, a quite different outcome was observed in a deceptively similar system. Thus, when $\mathrm{[Li\{CH(R)Ph\}(tmen)]}$ was treated with 2 ArNC at low temperature in pentane the product (xi in Scheme 1) was the red, crystalline 1-azabuta-1,3-dienyl-3-amido compound **8**. The formation of **8**, rather than that of an isomeric lithium β-diketiminate, may have been favoured by its extended conjugation; this feature was retained upon its protonolysis with methanol to yield (xii in Scheme 1) the corresponding yellow amine **9**.

Each of the lithium 1-azaallyls or β-diketiminates **1**, **2**, **6a**, **6b**, **6c** and **7** was both highly air-sensitive (hydrolysing readily) and soluble in hydrocarbons, the phenyl-substituted derivatives slightly less so than their trimethylsilyl analogues. The air-sensitive lithium amide **8** and the zirconium β-diketiminates **3** and **4** were insoluble or only sparingly soluble in pentane, and required diethyl ether or thf to dissolve significant amounts of each.

In our preliminary publication dealing with the synthesis of the lithium β-diketiminates **1** and **2** from $\mathrm{LiCHR_2}$ and $\mathrm{Bu^tNC}$ or ArNC respectively, we noted that the C–C-bond-making reactions also involved 1,2 shifts of a trimethylsilyl group and that a 1-azaallyllithium compound was probably implicated in the reaction pathway.[12] Having now isolated not only examples of the latter, **6a**–**6c**, but also the azabutadienylamidolithium compound **8**, we now suggest a more comprehensive rationalisation, illustrated in Scheme 2 for the case of $\mathrm{[Li\{CH(R)R'\}(tmen)]}$ and ArNC as reagents. The first step is envisaged to be formation of the nitrile–lithium alkyl donor–acceptor adduct **L**, which rearranged successively to the lithio-aldimine **M** and, consequent upon a 1,2-$\mathrm{Me_3Si}$ shift, the lithium 1-azaallyl **6**. When one of the three latter compounds, namely **6a**, was subjected to treatment with a further equivalent of ArNC, we presume that this proceeded *via* a further 1 : 1 adduct, analogous to **L** (not shown in Scheme 2), which rearranged to the intermediate **N** (related to **M**) and thence by a 1,2-$\mathrm{Me_3Si}$ shift to the lithium β-diketiminate **2**. When the initial reaction was between the lithium alkyl and 2 ArNC, we suggest that **M** rapidly reacted with the second equivalent of ArNC to form the 1 : 1 adduct **O**, which was transformed into **P** (a process similar to **L**→**M**). Thus, we envisage that the conversion of **M** into **O** is faster than its isomerisation into **6**. The successive rearrangement **O** into **P** and thence by a 1,2-$\mathrm{Me_3Si}$ shift into **8** completes the reaction sequence.

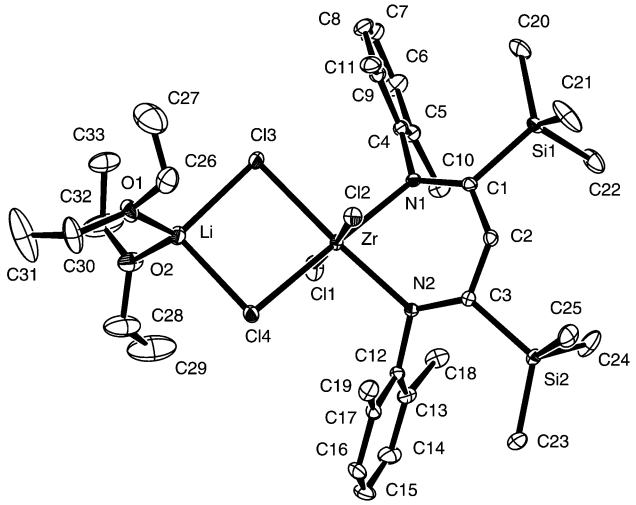


Fig. 1 The molecular structure of the crystalline complex **4**.

Although isocyanohydrocarbon adducts of transition metal complexes are well documented, analogues with main group metals are rare, but **H**[14] may be regarded as a model for **L** and **O**. The lithioaldimine **N**, like its analogue **P**, corresponds to the frequently postulated intermediate in C–C coupling reactions of the type referred to in the first paragraph of the present paper,[1–8] while 1,2-$\mathrm{Me_3Si}$ C→C shifts in appropriate carbanions are well established.[19]

Crystal structures of complexes 4, 6b and 8

The molecular structures of complexes **4**, **6b**, and **8** with the atom numbering schemes are shown in Figs. 1–3, respectively. Selected bond distances and angles are listed in Tables 1–3.

The β-diketiminatozirconium(iv) complex **4** (Fig. 1) was crystallised from diethyl ether as a monomeric heterobinuclear species in which the two metal atoms are bridged by the chloride atoms Cl(3) and Cl(4). The zirconium atom is in an approximately octahedral configuration, the two terminal chloride atoms Cl(1) and Cl(2) occupy axial positions, Cl(1)–Zr–Cl(2) 176.04(3)°, and the *cisoid* bond angles at zirconium range from 82.02(9) to 96.74(4)°. The lithium atom is in a distorted tetrahedral configuration, the bond angles at lithium ranging from 92.2(2) [Cl(3)–Li–Cl(4)] to 120.2(3)° [O(2)–Li–Cl(3)]. The Li–O and Li–Cl bond lengths and the angles

Table 1 Selected bond distances (Å) and angles (°) of complex **4**

Zr–N(1)	2.216(3)	Zr–N(2)	2.209(2)
Zr–Cl(1)	2.421(1)	Zr–Cl(2)	2.441(1)
Zr–Cl(3)	2.518(1)	Zr–Cl(4)	2.528(1)
Li–O(1)	1.919(6)	Li–O(2)	1.913(6)
Li–Cl(3)	2.399(6)	Li–Cl(4)	2.415(6)
Si(1)–C(1)	1.941(3)	Si(2)–C(3)	1.939(3)
N(1)–C(1)	1.335(4)	N(2)–C(3)	1.340(4)
N(1)–C(4)	1.455(4)	C(1)–C(2)	1.407(4)
N(2)–C(12)	1.456(4)		
N(2)–Zr–N(1)	82.02(9)	N(2)–Zr–Cl(1)	92.66(7)
N(1)–Zr–Cl(1)	95.77(7)	N(2)–Zr–Cl(2)	89.64(7)
N(1)–Zr–Cl(2)	87.74(7)	Cl(1)–Zr–Cl(2)	176.04(3)
N(2)–Zr–Cl(3)	176.33(7)	N(1)–Zr–Cl(3)	94.37(7)
Cl(1)–Zr–Cl(3)	87.04(4)	Cl(2)–Zr–Cl(3)	90.87(4)
N(2)–Zr–Cl(4)	96.74(7)	N(1)–Zr–Cl(4)	176.16(7)
Cl(1)–Zr–Cl(4)	87.91(4)	Cl(2)–Zr–Cl(4)	88.62(3)
Cl(3)–Zr–Cl(4)	86.91(3)	O(2)–Li–O(1)	114.3(3)
O(2)–Li–Cl(3)	120.2(3)	O(1)–Li–Cl(3)	107.2(3)
O(2)–Li–Cl(4)	109.9(3)	O(1)–Li–Cl(4)	110.8(3)
Cl(3)–Li–Cl(4)	92.2(2)		

Table 2 Selected bond distances (Å) and angles (°) of complex **6b**

Li–N(1)	1.946(10)	Li–N(2)	2.119(10)
Li–N(3)	2.075(11)	Li···C(8)	2.602(10)
Si–C(1)	1.909(5)	N(1)–C(1)	1.363(6)
N(1)–C(12)	1.420(6)	C(1)–C(2)	1.376(6)
C(2)–C(3)	1.457(6)	C(3)–C(8)	1.398(7)
C(3)–C(4)	1.414(7)	C(4)–C(5)	1.380(7)
C(5)–C(6)	1.390(7)	C(6)–C(7)	1.369(7)
C(7)–C(8)	1.400(7)		
N(1)–Li–N(3)	133.9(5)	N(1)–Li–N(2)	131.5(5)
N(3)–Li–N(2)	88.0(4)	C(1)–N(1)–C(12)	117.8(4)
C(1)–N(1)–Li	115.0(4)	C(12)–N(1)–Li	125.8(4)
N(1)–C(1)–C(2)	122.4(4)	N(1)–C(1)–Si	123.0(3)
C(2)–C(1)–Si	113.9(4)	C(1)–C(2)–C(3)	130.2(5)

Table 3 Selected bond distances (Å) and angles (°) of complex **8**

Li–N(1)	2.130(6)	Li–N(2)	1.970(6)
Li–N(3)	2.192(6)	Li–N(4)	2.214(6)
Si–C(1)	1.945(4)	N(1)–C(1)	1.297(4)
N(1)–C(10)	1.424(4)	N(2)–C(2)	1.355(4)
N(2)–C(18)	1.398(4)	C(1)–C(2)	1.502(5)
C(2)–C(3)	1.380(5)	C(3)–C(4)	1.454(5)
C(4)–C(9)	1.391(5)	C(4)–C(5)	1.402(5)
C(5)–C(6)	1.379(6)	C(6)–C(7)	1.375(6)
C(7)–C(8)	1.387(6)	C(8)–C(9)	1.380(5)
N(2)–Li–N(1)	80.2(2)	N(2)–Li–N(3)	114.4(3)
N(1)–Li–N(3)	127.2(3)	N(2)–Li–N(4)	140.9(3)
N(1)–Li–N(4)	118.2(3)	N(3)–Li–N(4)	83.0(2)
C(1)–N(1)–C(10)	122.8(3)	C(1)–N(1)–Li	113.0(3)
C(10)–N(1)–Li	124.0(3)	C(2)–N(2)–C(18)	119.6(3)
C(2)–N(2)–Li	115.8(3)	C(18)–N(2)–Li	120.8(3)
N(1)–C(1)–C(2)	115.2(3)	N(1)–C(1)–Si	125.0(3)
C(2)–C(1)–Si	119.8(2)	N(2)–C(2)–C(3)	128.6(3)
N(2)–C(2)–C(1)	115.7(3)	C(3)–C(2)–C(1)	115.5(3)
C(2)–C(3)–C(4)	130.9(3)		

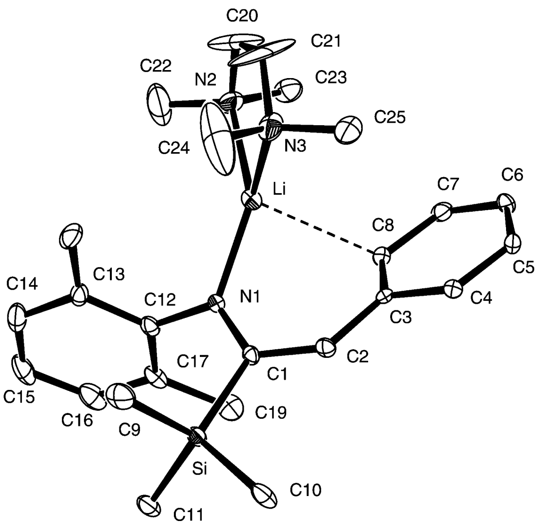


Fig. 2 The molecular structure of the crystalline complex **6b**.

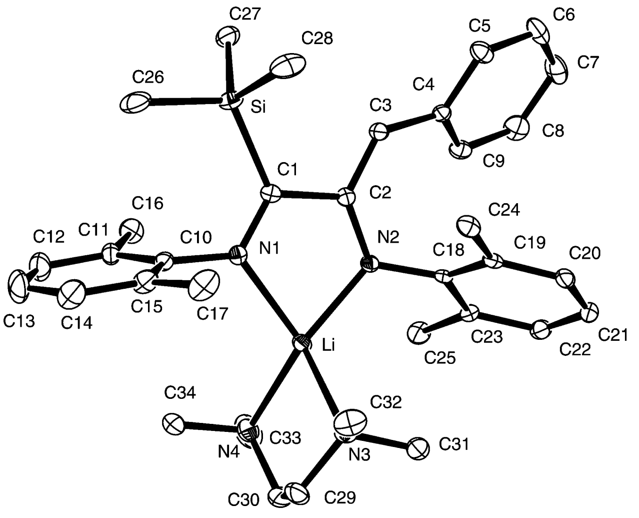
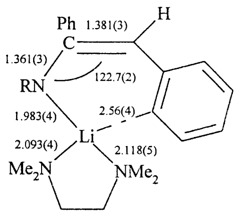


Fig. 3 The molecular structure of the crystalline complex **8**.

subtended at the lithium atom are very similar to those in the complexes **K**,[18a] **K′**,[18b] and **K″**.[18c] As in **K**, the terminal Zr–Cl bond lengths [mean 2.431(1) in **4** and 2.453 Å in **K**[18a]] are shorter than the bridging [mean 2.523(6) (**4**) and 2.561(6) Å in **K**[18a]]. The six-membered metallacycle $\overline{\mathrm{ZrN(1)C(2)C(3)N(2)}}$ adopts a boat conformation, but the transannular Zr···C(2) distance of 3.425(5) Å is much longer than the 2.54(1) or 2.703(2) Å in $[\overline{\mathrm{ZrCl_3\{N(R)C(Bu^t)C(H)C(Ph)N}}\mathrm{R\}}]$ **Q**[20] or $[\overline{\mathrm{Zr}(\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Cl_2\{N(Ph)(CH)_3N}}\mathrm{Ph\}}]$,[21] respectively, probably because **4**, unlike these, is coordinatively saturated at the zirconium atom. For the latter compounds, the β-diketiminato ligand has been described as having η^5-character, and thus is isoelectronic with an η^5-cyclopentadienyl; consistent with this view, the above trichloride with methylaluminoxane was shown to be an efficient ethylene polymerisation catalyst.[22] There is effective electron delocalisation in **4**, as evident from the similarity in each pair of Zr–N and N–C average bond lengths: 2.213(8) and 1.338(8) Å, respectively. These distances may be compared with the corresponding values in **Q** of 2.17(4) and 1.34(2) Å;[20] the central C–C bond distance in each is also similar, 1.407(4) and 1.42(1) Å in **4** and **Q**,[20] respectively.

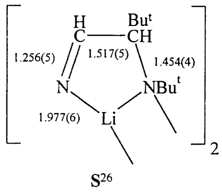
The crystalline 1-azaallyl compound **6b** (Fig. 2) is monomeric. The sum of the angles subtended by the three nitrogen atoms at the lithium atom is 354.2°. The deviation from planarity may be due to a short (agostic) Li···C contact of 2.60(1) Å involving an *o*-phenyl carbon atom, C(8); it may be compared with 2.23(2) and 2.32(2) Å for the α- and β-Li–C bonding distances, respectively in $[\mathrm{Li\{N(R)C(C_6H_4Br\text{-}4)CR_2\}(thf)}]$.[23] The nitrogen atom of the 1-azaallyl ligand, N(1), has the shorter Li–N distance [1.946(10) Å] compared with those of the chelating tmen: Li–N(2 or 3) = 2.097 ± 0.022 Å. The 1-azaallyl ligand is bonded to the lithium atom as the eneamido (rather than the η^3-1-azaallyl) tautomer, as evident additionally from the rather long N(1)–C(1) and short C(1)–C(2) distances of 1.363(6) and 1.376(6) Å, appropriate for single and double bonds, respectively, the wide N(1)–C(1)–C(2) angle of 122.4(4)° and the long separation between the lithium atom and C(1) and C(2) of 2.81(1) and 3.08(1) Å, respectively. The geometric parameters of **6b** are closely similar to those of **R**[9] and of $[\mathrm{Li\{N(R)C(C_6H_4Br\text{-}4){=}CR_2\}(thf)}]$,[23] whereas the corresponding distances of 2.571(8) and 2.724(8) Å in the binuclear



R[9]

1-azaallyllithium compound of eqn. (3) and its Li–N bond length of 1.957(8) Å are indicative of η^3-bonding.[16a] The arrangement about C(1)–C(2) in **6b** is *E*; *i.e.* the Ph and SiMe$_3$ groups are arranged in a *transoid* fashion.

The crystalline 1-azabuta-1,3-dienyl-3-amidolithium complex **8** (Fig. 3) is a monomer, in which the four-coordinate lithium atom is the spiro centre of a distorted tetrahedron, the two endocyclic angles subtended at the lithium atom, being bite angles, are inevitably acute, 80.2(2) and 83.0(2)° for N(1)–Li–N(2) and N(3)–Li–N(4), respectively. The $\overline{\mathrm{LiN(1)C(1)C(2)N(2)}}$ metallacycle is planar, only C(2) deviating by 0.002 Å from the mean plane. The dihedral angles between the two *N*,*N′*-aryl planes and this plane are 85.7(1) and 64.2(1)°, the two aryl substituents being mutually *transoid*. One short [Li–N(2), 1.970(6) Å] and three longer Li–N bond distances [2.130(6), 2.192(6) and 2.214(6) Å for Li–N(1, 3 and 4, respectively)], and the alternating bond distances of the anionic ligand [1.297(4), 1.502(5), 1.355(4) and 1.380(5) Å, for N(1)–C(1), C(1)–C(2), N(2)–C(2) and C(2)–C(3), respectively] indicate that the negative charge is mainly localised at N(2). This is consistent with the notion that complex **8** is a substituted lithium amide, stabilised by a transannular Li–N(aryl) and chelating *N*,*N′*-tmen dative bonds. We note that a typical Li–N(aryl) amide bond length in a monomeric datively bound complex is close to that for Li–N(2) in **8**, namely 1.895(8) Å in [Li{N(H)Ph}-(tmen)][24] or 2.00(1) Å in [Li{N(C$_{10}$H$_7$-1)Ph}(pmdien)].[25] Comparison between some of the geometric parameters of **8** with those of the binuclear complex **S**[26] is also informative.

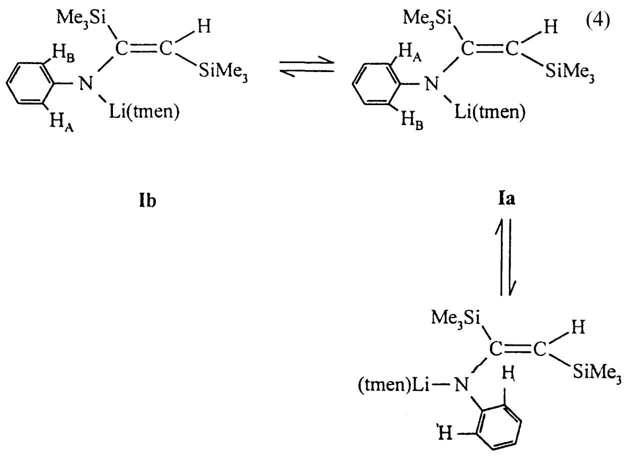


S[26]

NMR spectra and solution behaviour

The ^{1}H NMR spectrum of compound **6a** in C$_7$D$_8$ or C$_6$D$_6$ solution at room temperature showed the presence of two sets of signals indicating a mixture of two rotamers **Ia,b** and **II** in the approximate ratio of 4 : 1, (eqn. 4), with a coalescence temperature of 303 K. A second exchange process with a coalescence temperature of 193 K was observed for the major isomer, corresponding to the freezing of the rotation of the aryl group around the N–C bond, thereby making the *o*-methyl groups A and B at the aryl substituent magnetically different. The minor isomer showed no signs of such behaviour above 177 K. As delocalisation of π-electron density within the ligand may be more efficient if the aryl group is remote from the C=C double bond (rotamer **Ia,b**) and hence the N–C(aryl) bond for **Ib** may have the higher double bond character, we suggest that the rotation around this bond would be frozen out at a higher temperature than in isomer **II**. Thus, it seems likely that rotamer **Ia,b** is the major isomer.

The ^{1}H NMR spectra of solutions of complex **6b** or **6c** in C$_7$D$_8$ at room temperature showed only signals of one isomer for each. The chemical shift values for the PhC*H* protons (δ 5.39 for **6b** and δ 4.99 for **6c**) indicate that each has

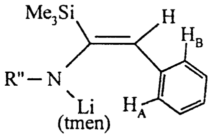


(4)

Ib **Ia**

II

the enamido type of structure similar to that observed in the solid state for **6b** (*cf.* also refs. 9 and 27) with the Ph substituent being *trans* to the SiMe$_3$ group (*cf.* **III**). This was supported for



III

both compounds by ^{1}H ^{6}Li-NOE-difference spectra which showed a close contact between the *trans*-butyl group (for **6c**, 9% NOE enhancement) or the aryl methyl groups (for **6b**, 8% NOE enhancement), NMe (24 or 27% NOE enhancement, respectively) and the *ortho*-H (11 or 19% NOE, respectively) of the phenyl substituent but not to the olefinic hydrogen atom. The major difference between the ^{1}H NMR spectra of **6b** and **6c** was that the signal for the two *ortho*-H atoms of the phenyl substituent at δ 8.0 was much broader for complex **6c** than for **6b** indicating hindered rotation around the C–C(*ipso*) bond. When a sample of **6c** was cooled to 208 K (coalescence temperature 223 K, corresponding to $\Delta G^{\#}_{223\ \mathrm{K}} = 39.9$ kJ mol^{-1}), the *o*-^{1}H signal split into two distinct doublets at δ 9.35 and 6.68. This assignment for the two hydrogen atoms was also supported by a homonuclear NOE experiment at 193 K which showed H(B) to be interacting strongly with PhC*H* but not H(A). A weakening of the C–H(A) bond, indicated by a reduction of the CH(A) coupling constant (consistent with an agostic Li–H–C interaction) was, however, not observed, $^1J(^{13}\mathrm{C}–^1\mathrm{H}) = 153$ or 152 Hz for C–H(A) and C–H(B). When the temperature was raised, the rate of rotation around the C–C(*ipso*) bond was increased until at 323 K only a slightly broadened singlet at δ 8.06 was observed. In the case of the sterically less hindered complex **6b** the rotation already at room temperature was so fast that only one sharp doublet was noted; only when **6b** was cooled, the signal began to broaden until at 178 K it separated into two singlets at δ 9.03 and *ca.* δ 7.0 (obscured by other signals in this region; coalescence temperature 193 K).

A hindered rotation around the N–C(*ipso*) bond, as found for complex **6a** (*cf.* rotamers **Ia** and **Ib**) was not observed for **6b** even at lower temperatures.

The NMR spectra of the other reported compounds showed no unusual noteworthy features.

Experimental

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. The NMR spectra were recorded in C$_6$D$_6$ or

C_7D_8 at 298 K using the following Bruker instruments: DPX 300 (^{1}H, 300.1; ^{13}C, 75.5; ^{7}Li, 116.6 MHz) and AMX 500 (^{1}H, 500.1; ^{13}C, 125.7; ^{29}Si, 99.4 MHz) and referenced internally to residual solvent resonances (data in δ) in the case of ^{1}H and ^{13}C spectra. The ^{7}Li and ^{29}Si spectra were referenced externally to LiCl and $SiMe_4$, respectively. Unless otherwise stated, all NMR spectra other than ^{1}H were proton-decoupled. Electron impact mass spectra were from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected. Elemental analyses were determined by Medac Ltd., Brunel University, Uxbridge, UK.

Preparations

$[\overline{\mathrm{Li\{N(Bu^t)C(R)C(H)C(R)N}}\mathrm{(Bu^t)\}][LiC(H)R_2](CNBu^t)}$ 1. Bu^{t}NC (1.2 cm^3, 10 mmol) was added to a solution of $LiCH(SiMe_3)_2$ (1.17 g, 7.03 mmol) in Et_2O at −40 °C. (The chosen stoichiometry was optimal, based on several alternatives.) The reaction mixture was slowly warmed to room temperature and then stirred for a further 15 h. The solvent was removed *in vacuo* and "stripped" with pentane. The obtained sticky, yellow residue was heated for 4 h at 60 °C *in vacuo*; then extracted into pentane (80 cm^3). The filtered extract was concentrated and cooled, yielding yellow crystals of **1** (0.68 g, 33% based on Li) (Found: C, 59.0; H, 11.60; N, 7.20. $C_{29}H_{65}Li_2N_3Si_4$ requires C, 59.0; H, 11.49; N, 7.37%), mp 137 °C (decomp.). ^{1}H NMR (C_6D_6): δ −1.69 (s, C*H*Si$_2$, 1 H), 0.41 (s, SiMe$_3$, 18 H), 0.52 (s, SiMe$_3$, 18 H), 0.72 [s, Bu^t (CNBu^t), 9 H], 1.42 (s, Bu^t, 18 H), 5.40 (s, CH, 1 H); ^{7}Li NMR (C_6D_6): δ 0.8; ^{13}C NMR (C_6D_6): δ 3.3 (s, *C*HSi$_2$), 4.4 (s, SiMe$_3$), 7.3 (s, SiMe$_3$), 29.4 [s, C(*C*H$_3$)$_3$ (CNBu^t)], 32.8 (s, C(*C*H$_3$)$_3$), 54.7 (s, *C*(CH$_3$)$_3$), 55.9 [s, *C*(CH$_3$)$_3$ (CNBu^t)], 108.5 (s, CH), 142.3 [s, CN (CNBu^t)], 179.9 (s, CN). The mass spectrum was not informative.

$[\overline{\mathrm{Li\{N(C_6H_3Me_2\text{-}2,6)C(R)C(H)C(R)N}}\mathrm{(C_6H_3Me_2\text{-}2,6)\}]}$ 2. Solid $C_6H_3(Me_2\text{-}2,6)NC$ (3.15 g, 2.4 mmol) was added to a suspension of $LiCH(SiMe_3)_2$ (2.0 g, 1.2 mmol) in pentane (100 cm^3) and Et_2O (0.1 cm^3) at −78 °C. The mixture was allowed to warm to room temperature during a period of 15 h (in a plastic bowl filled with acetone/dry ice). A dark red solution with a small amount of white precipitate was obtained. After removing the solvent and extracting the residue into pentane (60 cm^3), the mixture was filtered and the filtrate concentrated and cooled affording orange crystals of **2** which were contaminated by a small amount of free isocyanide. The latter was sublimed off by heating the sample for 1 h to 120 °C *in vacuo* leaving **2** (3.41 g, 66.3%) (Found: C, 69.9; H, 8.51; N, 6.67. $C_{25}H_{37}LiN_2Si_2$ requires C, 70.0; H, 8.70; N, 6.53%), mp 210 °C (decomp.). Mass spectrum [*m*/*z* (%)]: 422 (6 [M − Li]$^+$), 407 (3 [M − Li − Me]$^+$), 349 (19 [M − Li − SiMe$_3$]$^+$). ^{1}H NMR (C_6D_6): δ 0.05 (s, SiMe$_3$, 18 H), 2.03 (s, Me, 12 H), 5.48 (s, CH, 1 H), 6.90–6.92 (Ph, 4 H), 6.99–7.01 (Ph, 6 H); ^{7}Li NMR (C_6D_6): δ 0.8; ^{13}C NMR (C_6D_6): δ 1.34 (s, SiMe$_3$), 19.4 (s, Me), 104.6 (s, CH), 122.5 and 127.9 (s, *m*/*p*-C), 131.2 (s, *o*-C), 154.0 (s, *ipso*-C), 172.3 (s, CN).

$[\overline{\mathrm{Zr\{N(Bu^t)C(R)C(H)C(R)N}}\mathrm{(Bu^t)\}Cl_3]}$ 3. $ZrCl_4$ (0.27 g, 1.17 mmol) was added to a solution of **1** (0.68 g, 1.17 mmol) in Et_2O (20 cm^3) at −30 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 14 h. The volatiles were removed *in vacuo*. The residue was extracted into pentane (30 cm^3) and the extract was filtered. Concentration of the filtrate and cooling gave pale yellow crystals of **3** (0.26 g, 42.5%) (Found: C, 37.9; H, 7.19; N, 5.05. $C_{17}H_{37}Cl_3N_2Si_2Zr$ requires C, 39.0; H, 7.13; N, 5.35%), mp > 120 °C (decomp.). Mass spectrum [*m*/*z* (%)]: 522 (38 [M]$^+$), 507 (45 [M − Me]$^+$), 487 (43 [M − Cl]$^+$), 465 (95 [M − CMe$_3$]$^+$), 449 (18 [M − SiMe$_3$]$^+$). ^{1}H NMR (C_6D_6): δ 0.26 (s, SiMe$_3$, 18 H), 1.39 (s, Bu^t, 18 H), 6.42 (s, CH, 1 H); ^{13}C NMR (C_6D_6): δ 2.2 (s, SiMe$_3$), 31.9 (s, C(*C*H$_3$)$_3$), 60.6 (s, *C*(CH$_3$)$_3$), 98.6 (s, CH), 162.0 (s, CN).

$[\overline{\mathrm{Zr\{N(Ar)C(R)C(H)C(R)N}}\mathrm{(Ar)\}Cl_2(\mu\text{-}Cl)_2Li(OEt_2)_2]}$ 4. $ZrCl_4$ (0.37 g, 1.59 mmol) was added at −78 °C to a solution of **2** (0.68 g, 1.59 mmol) in Et_2O (30 cm^3). The reaction mixture was allowed to warm to room temperature and was stirred for 14 h yielding an orange suspension, which was filtered to remove a small amount of solid and cooled to give yellow crystals of **4** (0.81 g, 63%). Another crop of **4** (0.30 g, 23.2%) (Found: C, 47.9; H, 6.97; N, 3.89. $C_{33}H_{57}Cl_4LiN_2O_2Si_2Zr$ requires C, 48.9; H, 7.09; N, 3.45%) was obtained from the mother liquor. Mass spectrum [*m*/*z* (%)]: 618 (20 [M − LiCl(Et$_2$O)$_2$]$^+$), 603 (7 [M − LiCl(Et$_2$O)$_2$ − Me]$^+$), 583 (10 [M − LiCl(Et$_2$O)$_2$ − Cl]$^+$), 545 (25 [M − LiCl(Et$_2$O)$_2$ − SiMe$_3$]$^+$), 509 (7 [M − LiCl(Et$_2$O)$_2$ − Ar]$^+$), 421 (73 [Ar]$^+$). ^{1}H NMR (C_6D_6): δ −0.05 (s, SiMe$_3$, 18 H), 1.19 [t, CH$_3$ (Et$_2$O), 12 H, $^3J(^1\text{H}–^1\text{H}) = 7.1$], 2.34 (s, Me, 12 H), 3.62 [q, OCH$_2$, 8H, $^3J(^1\text{H}–^1\text{H}) = 7.1$ Hz], 6.60 (s, CH, 1 H), 7.04 (s, broad, Ph, 6 H); ^{13}C NMR (C_6D_6): δ 0.6 (s, SiMe$_3$), 14.2 [s, Me (Et$_2$O)], 20.4 (s, Me), 66.4 (s, OCH$_2$), 116.3 (s, CH), 122.9 (s, *p*-C), 128.6 (s, *m*-C), 134.9 [s, *ipso*-C (Me)], 146.7 (s, *ipso*-C), 179.6 (s, CN).

$[\overline{\mathrm{HN(C_6H_3Me_2\text{-}2,6)C(R)C(H)C(R)N}}\mathrm{(C_6H_3Me_2\text{-}2,6)}]$ 5. Methanol (0.07 cm^3, 1.61 mmol) was added to a solution of **2** (0.69 g, 1.61 mmol) in pentane (40 cm^3). The colour changed from red to yellow and a white precipitate was formed. The mixture was stirred for 15 h at room temperature and then filtered. Concentration of the filtrate and cooling gave yellow needles of **5** (0.33 g, 48.5%). A second crop of crystals (0.22 g, 32.3%) (Found: C, 69.8; H, 8.81; N, 6.66. $C_{25}H_{38}N_2Si_2$ requires C, 71.0; H, 9.06; N, 6.62%), mp 131 °C (decomp.) was isolated from the mother liquor. Mass spectrum [*m*/*z* (%)]: 422 (60 [M]$^+$), 407 (35 [M − Me]$^+$), 349 (100 [M − SiMe$_3$]$^+$), 317 (45 [M − Ar]$^+$). ^{1}H NMR (C_6D_6): δ −0.01 (s, SiMe$_3$, 18 H), 2.18 (s, Me, 12 H), 5.71 (s, CH, 1H), 6.92 (s, broad, Ph, 12 H), 13.26 (s, NH, 1 H); ^{13}C NMR (C_6D_6): δ −0.1 (s, SiMe$_3$), 18.9 (s, Me), 105.5 (s, CH), 125.0, 128.5 (s, *m*/*p*-C), 132.6 [s, *ipso*-C (Me)], 146.4 (s, *ipso*-C), 172.1 (s, CN).

$[\mathrm{Li\{N(C_6H_3Me_2\text{-}2,6)C(R)C(H)R\}(tmen)}]$ 6a. $LiCH(SiMe_3)_2$ (0.44 g, 2.65 mmol) was dissolved in a mixture of pentane (30 cm^3) and tmen (0.40 cm^3, 2.65 mmol). The mixture was cooled to −90 °C and $(C_6H_3Me_2\text{-}2,6)NC$ (0.35 g, 2.65 mmol) was added. After allowing the mixture to warm to room temperature during a period of 3 h it was stirred for a further 12 h; a dark green solution was obtained. After removing all volatiles *in vacuo* and extracting the residue with pentane the red extract was filtered. Upon cooling the filtrate dark red crystals of **6a** (0.73 g, 66.6%), mp 62 °C (decomp.) were obtained. Mass spectrum [*m*/*z* (%)]: (L$^-$ = anionic ligand) 291 (55 [HL]$^+$), 276 (45 [HL − Me]$^+$), 218 (86 [HL − SiMe$_3$]$^+$), 204 (80 [ArN=CSiMe$_3$]$^+$), 186 (53 [HL − Ar]$^+$), 116 (57 [tmen]$^+$). ^{1}H NMR (C_7D_8) (values for rotamer **II** in brackets): δ 0.03 (0.30) [s, CHSi*Me*$_3$, 9 H], 0.20 (0.34) (s, SiMe$_3$, 9 H), 1.42 (s, NCH$_2$, 4 H), 1.51 (s, NMe, 12 H), 2.31 (2.24) (s, Me, 6 H), 3.8 (s, CH, 1 H), 6.80–7.15 (Ph, 3 H); ^{7}Li NMR (C_7D_8): δ 0.51; ^{13}C NMR (C_7D_8): δ 0.6 (1.9) [s, SiMe$_3$], 3.0 (4.6) [s, SiMe$_3$], 20.3 (19.1) [s, Me], 45.3 [s, NMe], 56.5 [s, NCH$_2$], 84.7 (83.7) [s, CH], 120.0 (120.5) [s, *p*-C], 128.7 (128.1) [s, *m*-C], 129.2 (132.4) [s, *ipso*-C (Me)], 156.5 (154.7) [s, *ipso*-C], 172.2 and 169.8 [s, CN].

The signals of the two rotamers in solution were assigned by NOE ^{1}H NMR experiments involving the protons of the trimethylsilyl, aryl methyl, and olefinic CH groups.

[Li{N(Ar)C(R)C(H)Ph}(tmen)] 6b. $C_6H_3(Me_2\text{-}2,6)NC$ (2.24 g, 17 mmol) was added to a solution of [Li{CH(R)Ph}(tmen)] (4.90 g, 17 mmol) in Et_2O (150 cm^3) at −60 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 14 h to give a pale red suspension which was filtered. Concentration and cooling of the filtrate gave **6b** (5.00 g, 70%). A second crop of crystals of **6b** (0.86 g, 12%) (Found: C, 70.5;

H, 9.13; N, 9.62; $C_{25}H_{40}LiN_3Si_3$ requires C, 71.9; H, 9.65; N, 10.06%), mp 135 °C (decomp.) was isolated from the mother liquor. Mass spectrum [*m*/*z* (%)]: 295 (20 $[HL]^+$), 280 (12 $[HL - Me]^+$), 222 (14 $[HL - SiMe_3]^+$), 204 (100 $[HL - C_7H_7]^+$). ^{1}H NMR (C_6D_6): δ 0.22 (s, $SiMe_3$, 9 H), 1.40 (s, NCH_2, 4 H), 1.54 (s, NMe, 12 H), 5.39 (s, CH, 1 H), 6.69 (t, Ph, 1 H), 6.92 (t, Ph, 1 H, $J = 7.35$), 7.08 (d, Ph, $J = 7.72$, 2 H), 7.17 (d, Ph, 2 H), 8.01 (d, Ph, $J = 7.77$ Hz, 2 H); ^{7}Li NMR (C_6D_6): δ 0.83; ^{13}C NMR (C_7D_8): δ 1.9 (s, $SiMe_3$), 20.3 (s, Me), 45.3 (s, NMe), 56.6 (s, NCH_2), 99.4 [s, CH; ^{1}H–coup., d, $^1J(^{13}C–^1H)$ 151.6], 118.9 [s, *p*-C(Ph); ^{1}H-coup., td, $^1J(^{13}C–^1H)$ 159.3], 119.7 [s, *p*-C(Ar); ^{1}H-coup., d, $^1J(^{13}C–^1H)$ 156.5], 123.3 [s, *o*-C(Ph); ^{1}H-coup., d, $^1J(^{13}C–^1H)$ 154.0], 128.2 [s, *m*-C(Ph); ^{1}H-coup., md, $^1J(^{13}C–^1H)$ 153.4], 129.9 [s, *m*-C(Ar); ^{1}H-coup., dd, $^1J(^{13}C–^1H)$ 154.5, $^3J(^{13}C–^1H)$ 8.0 Hz], 132.1 [s, *ipso*-C (ArMe)], 145.7 [s, *ipso*-C(Ph)], 157.1 [s, *ipso*-C (Ar)], 167.1 (s, CN).

[Li{N(Bu^t)C(R)C(H)Ph}(tmen)] 6c. Bu^{t}NC (0.39 cm^3, 3.50 mmol) was added at −50 °C to a solution of [Li{CH(R)Ph}-(tmen)] (1.0 g, 3.50 mmol) in Et_2O (30 cm^3). The yellow suspension was allowed to warm to room temperature; a clear solution was obtained. This was stirred for 14 h, the solvent was removed *in vacuo* and the residue was extracted into pentane (30 cm^3). Filtration of the extract and cooling of the filtrate to −30 °C gave **6c** (0.9 g, 69.6%) (Found: C, 67.6; H, 10.90; N, 11.42. $C_{21}H_{40}LiN_3Si$ requires C, 68.2; H, 10.91; N, 11.37%), mp 85 °C (decomp.). Mass spectrum [*m*/*z* (%)]: 369 (1 $[M]^+$); 247 (56 $[HL]^+$). ^{1}H NMR (C_6D_6): δ 0.48 (s, $SiMe_3$, 9 H), 1.47 (s, Bu^t, 9 H), 1.52 (s, NCH_2, 4 H), 1.72 (s, NMe, 12 H), 4.99 (s, CH, 1 H), 6.63 (t, *p*-Ph, 1 H), 7.85 (t, *m*-Ph, 2 H), 8.06 (s, broad, *o*-Ph, 2 H); ^{7}Li NMR (C_6D_6): δ −0.54; ^{29}Si NMR (C_6D_6): δ −15.8; ^{13}C NMR (C_6D_6): δ 4.3 (s, $SiMe_3$), 34.5 (s, C*Me*$_3$), 45.5 (s, NMe), 53.5 (s, *C*Me$_3$), 56.3 (s, NCH_2), 93.4 (s, CH), 117.3 (s, *p*-C), 122.3 (s, broad, *o*-C), 129.1 (s, *m*-C), 143.7 (s, *ipso-C*), 166.4 (s, CN).

[Li{N($C_6H_3Me_2$-2,6)C(R)C(H)C(Ph)N(R)}(tmen)] 7. PhCN (0.10 cm^3, 0.97 mmol) was added to a solution of **6a** (0.4 g, 0.97 mmol) in pentane (30 cm^3) at −40 °C. Upon warming up to room temperature a clear orange solution was obtained which was stirred for 15 h. Removing the volatiles *in vacuo* and extracting with pentane (60 cm^3) gave, upon concentrating and cooling to −30 °C, orange crystals of **7** (0.32 g, 64%) (Found: C, 64.2; H, 8.77; N, 8.98. $C_{29}H_{49}LiN_4Si_2$ requires C, 67.4; H, 9.56; N, 10.83%), mp 149 °C (decomp.). Mass spectrum [*m*/*z* (%)]: 394 (55 $[HL^+]$), 379 (10 $[HL - Me]^+$), 321 (90 $[HL - SiMe_3]^+$), 289 (26 $[HL - Ar]^+$). ^{1}H NMR (C_6D_6): δ 0.07 (s, $SiMe_3$, 9 H), 0.11 (s, $SiMe_3$, 9 H), 1.81 (s, NCH_2, 4 H), 1.91 (s, NMe, 12 H), 2.31 (s, Me, 6 H), 5.57 (s, CH, 1 H), 6.82–7.27 (Ph, 6 H), 7.74 [d, *o*-Ph, 2 H, $J(^1H–^1H) = 6.8$ Hz]; ^{7}Li NMR (C_6D_6): δ 1.45; ^{13}C NMR (C_6D_6): δ 1.0 (s, $SiMe_3$), 4.2 (s, $SiMe_3$), 19.4 (s, Me), 46.4 (s, NMe), 57.3 (s, NCH_2), 105.1 (s, CH), 122.3, 127.4, 127.8, 127.9, 128.8 (s, *m*/*p*-C), 130.3 [s, *ipso*-C(Me)], 150.8, 154.6 (s, *ipso*-C), 169.0, 177.9 (s, CN).

[Li{N($C_6H_3Me_2$-2,6)C(R)C[N($C_6H_3Me_2$-2,6)]=C(H)Ph}-(tmen)] 8. Solid ($C_6H_3Me_2$-2,6)NC (1.95 g, 15 mmol) was added to a suspension of [Li{CH(R)Ph}(tmen)] (2.13 g, 7.45 mmol) in pentane (150 cm^3) at −78 °C. The reaction mixture was allowed to warm up slowly (in a Dewar vessel) to room temperature. The red solution was stirred for 12 h, pentane (100 cm^3) was added and the mixture was filtered. The red precipitate was found to be analytically pure **8** (1.32 g, 32%) (Found: C, 74.85; H, 8.83; N, 11.65. $C_{34}H_{49}LiN_4Si$ requires C, 74.71; H, 9.00; N, 10.20%), mp 135 °C (decomp.). The filtrate was concentrated and two more crops of crystals of **8** (0.66 and 0.52 g, 16% and 12.7%) were isolated after cooling to −30 °C. Mass spectrum [*m*/*z* (%)]: 426 (60 $[HL]^+$), 411 (8 $[HL - Me]^+$). ^{1}H NMR (C_6D_6): δ 0.23 (s, $SiMe_3$, 9 H), 1.53 (s, broad, tmen, 16 H), 2.04, 2.34 (s, Me, 12 H), 6.10 (s, CH, 1 H), 6.69 (t, Ph, 1 H), 6.70–7.08 (Ph, 10 H); ^{7}Li NMR (C_6D_6): δ 1.44; ^{29}Si NMR (C_6D_6): δ −8.5; ^{13}C NMR (C_6D_6): δ 3.6 (s, $SiMe_3$), 18.9, 20.8 (s, Me), 45.8 (s, NMe), 57.3 (s, NCH_2), 110.0 (s, CH), 117.7, 122.2, 123.2, 126.5, 126.9, 127.5, 128.0, 128.3, 128.7 (s, Ph), 140.1, 152.6, 153.1 [s, *ipso*-C(Me)], 155.6 (s, *C*=CH), 195.4 (s, CN).

[HN($C_6H_3Me_2$-2,6)C(R)C{N($C_6H_3Me_2$-2,6)}=C(H)Ph] 9. Methanol (0.05 cm^3) was added to a suspension of **8** (0.66 g, 1.20 mmol) in pentane (30 cm^3). An immediate colour change from red to yellow and concomitant formation of a white precipitate were observed. After stirring for 10 min at room temperature all volatiles were removed *in vacuo*; the residue was extracted into pentane (30 cm^3). The extract was filtered and the filtrate concentrated and cooled to give yellow crystals of **9** (0.37 g, 79.4%) (Found: C, 78.8; H, 8.18; N, 6.50. $C_{28}H_{34}N_2Si$ requires C, 78.8; H, 8.17; N, 6.58%). Mass spectrum [*m*/*z* (%)]: 426 (37 $[M]^+$), 411 (8 $[M - Me]^+$), ^{1}H NMR (C_6D_6, all signals broad): δ 0.08 (s, $SiMe_3$, 9 H), 2.03 and 2.12 (s, Me, 12 H), 6.30 (s, CH, 1 H), 6.74–6.96 (s, Ph, 11 H), 7.47 (s, NH, 1 H); ^{13}C NMR (C_6D_6): δ 1.5 (s, $SiMe_3$), 18.5 and 19.3 (s, Me), 111.5 (s, Me), 123.2, 124.3, 125.6, 127.1, 128.0, 128.3, 128.5 (s, Ph), 132.7, 135.9, 139.7, 140.5 (s, *ipso*-C), 150.6 (s, *C*=CH), 180.1 (s, CN).

Crystal data and refinement details

$C_{33}H_{57}Cl_4LiN_2O_2Si_2Zr$ **4**, $M = 809.95$, monoclinic, $a = 14.838(3)$, $b = 15.446(3)$, $c = 19.174(4)$ Å, $\beta = 105.05(2)°$, $U = 4244(2)$ Å^3, $T = 173(2)$ K, space group $P2_1/n$ (no. 14), $Z = 4$, $D_c = 1.27$ Mg m^{-3}, μ(Mo-Kα) = 0.60 mm^{-1}, 7750 reflections measured, 7454 unique ($R_{int} = 0.017$), $R1 = 0.040$ for 5800 reflections with $I > 2\sigma(I)$, $wR2 = 0.105$ for all data.

$C_{25}H_{40}LiN_3Si$ **6b**, $M = 417.6$, monoclinic, $a = 32.900(7)$, $b = 8.553(2)$, $c = 19.852(5)$ Å, $\beta = 113.77(2)°$, $U = 5112(2)$ Å^3, $T = 173(2)$ K, space group $C2/c$ (no. 15), $Z = 8$, $D_c = 1.09$ Mg m^{-3}, μ(Mo-Kα) = 0.11 mm^{-1}, 4567 reflections measured, 4494 unique ($R_{int} = 0.052$), $R1 = 0.088$ for 2174 reflections with $I > 2\sigma(I)$, $wR2 = 0.222$ for all data.

$C_{34}H_{49}LiN_4Si$ **8**, $M = 548.8$, triclinic, $a = 10.887(3)$, $b = 11.272(2)$, $c = 14.266(3)$ Å, $\alpha = 87.11(2)$, $\beta = 76.64(2)$, $\gamma = 84.46(2)°$, $U = 1695(1)$ Å^3, $T = 173(2)$ K, space group $P\bar{1}$-(no. 2), $Z = 2$, $D_c = 1.08$ Mg m^{-3}, μ(Mo-Kα) = 0.10 mm^{-1}, 4698 reflections measured, 4698 unique, $R1 = 0.063$ for 3066 reflections with $I > 2\sigma(I)$, $wR2 = 0.178$ for all data.

Data were collected on an Enraf-Nonius CAD4 diffractometer using monochromatic Mo-Kα radiation (λ 0.71073 Å). Crystals were enclosed in an oil drop and frozen in a stream of cold nitrogen gas. Positions of non-hydrogen atoms were derived by direct methods using SHELXS-86[28] and refined on F^2 with anisotropic thermal parameters for non-hydrogen atoms and H atoms in riding mode, by full-matrix least-squares using SHELXL-93.[29]

CCDC reference numbers 165562–165564.

See http://www.rsc.org/suppdata/dt/b1/b103553n/ for crystallographic data in CIF or other electronic format.

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References

1 G. E. Niznik, W. H. Morrison and H. M. Walborsky, *J. Org. Chem.*, 1974, **39**, 600.
2 H. M. Walborsky, W. H. Morrison and G. E. Niznik, *J. Am. Chem. Soc.*, 1970, **92**, 6675.

3 M. J. Marks and H. M. Walborsky, *J. Org. Chem.*, 1981, **46**, 5404.
4 H. M. Walborsky and P. Ronman, *J. Org. Chem.*, 1978, **43**, 731.
5 H. M. Walborsky and G. E. Niznik, *J. Am. Chem. Soc.*, 1969, **91**, 7778.
6 N. Hirowatari and H. M. Walborsky, *J. Org. Chem.*, 1974, **39**, 604.
7 U. Schöllkopf and F. Gehrhart, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 805.
8 M. P. Periasamy and H. M. Walborsky, *J. Org. Chem.*, 1974, **74**, 611.
9 P. B. Hitchcock, M. F. Lappert, M. Layh, D.-S. Liu, R. Sablong and T. Shun, *J. Chem. Soc., Dalton Trans.*, 2000, 2301 and refs. therein.
10 M. Murakami, H. Masuda, T. Kawano, H. Nakamura and Y. Ito, *J. Org. Chem.*, 1991, **56**, 1.
11 A. C. Filippou, C. Völkl and P. Kiprof, *J. Organomet. Chem.*, 1991, **415**, 375.
12 P. B. Hitchcock, M. F. Lappert and M. Layh, *Chem. Commun.*, 1998, 201.
13 P. B. Hitchcock, M. F. Lappert and M. Layh, *Angew. Chem., Int. Ed.*, 1999, **38**, 501.
14 C. F. Caro, P. B. Hitchcock, M. F. Lappert and M. Layh, *Chem. Commun.*, 1998, 1297.
15 M. F. Lappert, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem Commun.*, 1982, 14.
16 (*a*) W.-P. Leung, H. Cheng, D.-S. Liu, Q.-G. Wang and T. C. W. Mak, *Organometallics*, 2000, **19**, 3001; (*b*) W.-P. Leung, H. Cheng, R.-B. Huang, Q.-C. Yang and T. C. W. Mak, *Chem. Commun.*, 2000, 451.
17 J. L. Atwood, W. E. Hunter, R. D. Rogers, J. Holton, J. McMeeking, R. Pearce and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1978, 140.
18 (*a*) T. V. Lubben, P. T. Wolczanski and G. D. Van Duyne, *Organometallics*, 1984, **3**, 977; (*b*) H. Memmler, K. Walsh, L. H. Gade and J. W. Lauher, *Inorg. Chem.*, 1995, **34**, 4062; (*c*) R. W. Quan, G. C. Bazan, A. F. Kiely, W. P. Schaefer and J. E. Bercaw, *J. Am. Chem. Soc.*, 1994, **116**, 4489.
19 *cf.*, R. West, *Adv. Organomet. Chem.*, 1977, **16**, 1.
20 M. F. Lappert and D.-S. Liu, *J. Organomet. Chem.*, 1995, **500**, 203.
21 M. Rahim, N. J. Taylor, S. Xin and S. Collins, *Organometallics*, 1998, **17**, 1315.
22 M. F. Lappert and D.-S. Liu, *Neth. Pat. Appl.*, 1994, 9401515.
23 M. F. Lappert and M. Layh, *Tetrahedron Lett.*, 1998, **39**, 4745.
24 T. Fjeldberg, P. B. Hitchcock, M. F. Lappert and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1984, 822.
25 D. Barr, W. Clegg, R. E. Mulvey, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1987, 716.
26 M. G. Gardiner and C. L. Raston, *Inorg. Chem.*, 1995, **34**, 4206.
27 P. B. Hitchcock, M. F. Lappert and M. Layh, *J. Chem. Soc., Dalton Trans.*, 1998, 1619.
28 G. M. Sheldrick, SHELXS-86 Program for the Solution of Crystal Structures, University of Göttingen, 1985.
29 G. M. Sheldrick SHELXL-93 Program for Crystal Structure Refinement, University of Göttingen, 1993.